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INTERIM DEVELOPMENT REPORT NO. 480-Q4

for

ELECTRO-OPTICAL MATRIX DISPLAY

This Report Covers The Period  
18 June 1965 to 18 September 1965

Solid State Electronics Laboratory  
Laboratory For Electronics, Inc.  
1075 Commonwealth Avenue  
Boston 15, Massachusetts

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This is the fourth quarterly Interim Development Report for the BuShips project under Contract No. NObsr-91199. The project is being performed by the Solid State Electronics Laboratory in the research and engineering division of LFE Electronics. The BuShips project is part of a total program on research in ferromagnetics with applications to new memory and display devices. The total program has LFE as well as Government support.

### Project Personnel

The BuShips project is under the direction of Dr. Robert J. Spain. The following personnel had assignments on the project in the reporting period:

Adamsky, Robert	192
Bardsley, Charles	192
Berghold, Robert	12
Deininger, Curtis	10
Denietolis, Vincent	4
Franklin, Dennis	68
Gee, Dick	6
Gould, Floyd	168
LeBlanc, Robert	110
Spain, Robert	30
Total	792

### Staff of the Solid State Electronics Laboratory

Adamsky, Robert F.	Senior Physical Chemist
Bardsley, Charles J.	Applied Scientist
Battarel, Claude P.	Senior Electronics Engineer
Berghold, Robert L.	Photographic Specialist

Staff of the Solid State Electronics Laboratory (continued)

Capell, William J.	Electronics Engineer
Choate, William	Technician
Chopourian, David	Senior Technician
Deininger, Curtis	Technician
Denietolis, Vincent N.	Designer
DiOrio, David R.	Engineering Assistant
Dussourd, Henry J.	Technician
Ferullo, Joseph F.	Engineering Assistant
Franklin, Dennis	Engineering Assistant
Fuller, Harrison W.	Mgr., Solid State Electronics Lab.
Gee, Dick	Physicist
Gorman, William T.	Senior Mechanical Engineer
ould, Floyd T.	Senior Physical Chemist
Horton, Charles E.	Engineering Assistant
Jauvtis, Harvey I.	Physicist
LeBlanc, Robert	Engineering Assistant
Lidman, Max	Technician
McCormack, Thomas L.	Senior Scientist
McLaughlin, Linda	Secretary
Morin, Maurice A.	Senior Chemist
Peoples, Patrick	Physicist
Pinkerton, Robert J.	Engineering Assistant
Shapiro, Herbert	Senior Chemist
Spain, Robert J.	Senior Physicist
Webber, Ronald J.	Applied Mathematician

## ABSTRACT

Preparation of RIS 1 films with low coercive force and good display properties is readily achieved, and continued efforts have been made toward further improvement of display element properties and reproducibility. The problem of immobilization of the bitter colloid in an unswitchable display pattern has been investigated by modifying the preparation of colloid dispersions, and by providing protective overlayers on the magnetic films. Recent non-aqueous suspensions in glycerine appear to be a solution to immobilization; other aqueous suspensions also show promising freedom from immobility over long periods. Protective coatings consisting of 3 layers of SiO of 800 Å, total thickness, appear effective in protecting films against corrosion and immobilization. Continued refinement of seals, spacers, and fil' ng techniques is in progress, although workable sealed modules can be readily made at the present state of development.

## 1.0 R I S FILM PREPARATION

Investigation of film deposition parameters has been continued with the intent of reducing film coercive force. Films made from a melt composition of about 83-17 Ni-Fe show low values of coercive force, and are usually slightly negatively magnetostrictive. However, since the film composition is close to the zero magnetostriction regions, such films often show no display property. The extreme sensitivity of film properties to composition in this region makes necessary strict control of evaporation conditions. The importance of evaporation rate and film thickness on the residual stress of the resultant film, and hence, on magnetic and display properties, has led to the installation of an Edwards Quartz Crystal Rate Monitor in the vacuum system. The monitor was tested under normal deposition conditions, and it was found that difficulties occurred because of interference from the induction generator. To overcome the pick-up of the RF signal, the leads of the monitor were shielded, greatly reducing the spurious signal. In addition, it is necessary to position the monitor so that only a portion of the large atom flux which is normally incident on the substrate reaches the monitor. Since a large portion of the period was devoted to tests of colloid solutions and protective overlayers, most of the films were made from 84-16 Ni/Fe melts in order to achieve a large number of bright display samples. These films are reasonably consistent in magnetic properties with  $H_c$  generally in the 6-9 oe range. Evaporation rates were  $\sim 100 \text{ \AA}/\text{minute}$  with substrate temperatures of 280-285°C.

### 1.1 X-ray Studies

The Philips X-ray Spectrograph was put into operation during the quarter, and test scans of display films showed only Ni and Fe as heavy metal components. Difficulties with a highly variable water supply have limited the use of the instrument to date; however, film composition will be monitored in the future as part of the effort to achieve high reproducibility. In addition, the apparatus

has been used as a diffractometer to obtain information on residual stress by line broadening techniques. Although first results show low intensities, it is believed that usable data can be obtained. The Hilger microfocus unit is also in operation, and will be used for photographic X-ray studies of film structure and stress.

## 2.0 PREPARATION OF THE DISPLAY COLLOID

The problem of immobilization of the colloidal particles due to sticking to the surface of the film was attacked in several different ways. The main effort was toward improving the colloidal magnetite in liquid systems. Other investigations included coating the particles with metallic copper, making two-component particles composed of silica and magnetite, and making particles by condensation from the vapor phase. Both ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) particles were coated with metallic copper by electroless deposition. Although the ferric oxide is non-magnetic, it was made magnetic by the coating. This was probably due to reduction of some of the ferric iron-to-ferrous iron by the plating solution, with subsequent formation of some magnetite ( $\text{Fe}_3\text{O}_4$ ), or by the formation of some copper ferrite ( $\text{CuO} \cdot \text{Fe}_2\text{O}_3$ ) which is magnetic. The coated particles were of a copper color and appeared to be the proper size, but were not compatible with any of the suspending mediums which were investigated. The two-component system composed of silica and magnetite was made by the hydrolysis of ferric chloride in the presence of colloidal silica (Cabosil) or by the addition of quaternary ammonium silicate to a ferric chloride solution. The quaternary ammonium silicate produced the best suspensions. The ferric oxide-silica particles were then made magnetic by reacting with ferrous carbonate. The product particles were approximately the right size and remained in colloidal suspension in slightly basic solution. This suggests that the silica coated the magnetite. However, the presence of the silica apparently catalyzed air oxidation of the magnetite ( $\text{Fe}_3\text{O}_4$ ) to ferric oxide ( $\text{Fe}_2\text{O}_3$ ), since, several days later, all of the particles had lost their magnetic property and had regained

the appearance of the original ferric oxide-silica material.

The formation of colloidal particles by condensation from the vapor phase produced the same results as was obtained with the copper coated particles. The particles were magnetic and most of them were of the proper size, but it was not possible to make a stable suspension of them.

All three of the approaches outlined above showed some promise, but all produced colloids which, it appeared, would be more difficult to suspend than magnetite ( $\text{Fe}_3\text{O}_4$ ) formed in liquid mediums. Moreover, improved magnetic films and new developments in suspending colloidal magnetite in non-aqueous mediums made it more desirable to proceed with the improvement of techniques which were in more advanced stages of development.

## 2.1 Suspensions in Non-Aqueous Liquids

Continuing developments in the formation and suspension of magnetite ( $\text{Fe}_3\text{O}_4$ ) in liquid mediums indicate that the best display colloids will be made and suspended in non-aqueous mediums. Electron micrographs of magnetite particles formed in acetone-methanol are of uniform particle size and the diffraction patterns are clearly that of magnetite. This is in contrast to many of the products from aqueous mediums which do not clearly show the magnetite pattern. Extended observation has disclosed that the colloid which contains relatively large crystallites of magnetite, as indicated by the diffraction pattern, is much more resistant to air oxidation than the ones which contain very small particles. Recently, a relatively large effort has been directed toward evaluating solutions containing particles which are made in aqueous mediums and which are subsequently transferred to non-aqueous mediums such as ethylene glycol and glycerine. The particles are made in the presence of a protecting agent (gelatin) in water and are dialyzed or leached free of soluble salts. The water content is then reduced by evaporation and is replaced with either ethylene glycol or glycerine. Evaluation is not complete, but results thus far are most



encouraging. The suspensions produce very bright diffraction patterns and have not shown any tendency to freeze when in contact with magnetic films. Test periods at present have been over two weeks. In addition, the non-aqueous medium renders all components non-biodegradable. These systems possess several additional advantages. They are non-ionic and thus much less corrosive; and, since both mediums (ethylene glycol and glycerine) do not evaporate, the sealing requirements are much less stringent. In addition, the demonstrated prolonged mobility on uncoated films may eliminate the coating requirement. Other non-aqueous non-volatile mediums are also under investigation as is the effect of adding sufficient water to the non-aqueous mediums to bring the vapor pressure of water over the solution up to ambient relative humidity. This would result in a medium which would neither gain nor lose water when exposed to air of that relative humidity. A second advantage gained by so doing is that the water content will lower the freezing point by about 40°C. The boiling point is also lowered somewhat, but this temperature is so high ( > 150°C) that the lowering is of no consequence.

The significant improvement in extension of mobility resulting from the use of the non-aqueous suspensions is considered to be a major advance in the development of the display unit. Life testing of sealed films containing such suspensions has so far covered over 16 days, and additional time will be required to properly evaluate this colloid; however, present results appear to be very promising. In addition to success in maintaining mobility with non-aqueous suspensions, several colloidal suspensions in water using dodecylamine as a suspending agent have shown long-term mobility in sealed units. Again, the time of testing has been insufficient to make a complete evaluation, but the suspensions have remained completely mobile while showing bright diffraction colors. These suspensions will probably require protective overlayers on the magnetic film to protect against corrosion.

## 2.2 Electron Microscope Studies

The Philips EM-75B electron microscope was employed for observation of colloidal particles as an aid in particle preparative techniques. Observations were made of particle and aggregate size, and also particle electron diffraction patterns. The freezing problem was investigated by direct stripping of solidified colloid on the display films. The observations of particle size in colloidal suspensions have shown the particle size variations which exist in individual solutions prepared by different methods. Particles have been generally observed to be 200-900 Å in size, with aggregates ranging from 2000-5000 Å. A typical aqueous colloid, containing gelatin, is shown in Figure 1. Extensive aggregation is observed, most of which results from the sample preparation technique used. This consisted of dispersion of a dilute solution of the colloid on a carbon substrate followed by rapid evaporation of the water, leaving the dried colloid particles on the carbon film. Electron diffraction of the colloidal suspensions indicated that the crystallites are generally very small, probably  $< 20$  Å, as indicated by the diffuse nature of the diffraction rings. Usually, one or two very broad diffraction rings are observed. In recent non-aqueous suspensions, sharper diffraction patterns result. These indicate that the particles are essentially magnetite,  $\text{Fe}_3\text{O}_4$ , and have crystallites of 50-200 Å in size. The data for a suspension prepared in acetone-methanol is shown below.

TABLE 1

<u>Diffraction Ring</u>	<u>d (measured)</u>	<u>d (magnetite)</u>
1	3.05	2.96
2	2.62	2.53
3	2.17	2.09
4	1.69	1.71
5	1.52	1.49

Some preparations in aqueous suspension show fibrous character which undoubtedly makes them unstable with respect to coagulation and immobilization.



Figure 1. Electron micrograph of aqueous colloid dispersion containing gelatin. 6000X

No consistent shape anisotropy has been found in colloids which show bright diffraction patterns, although such anisotropy might be beneficial.

Replicas of frozen and dried colloids collected on domain walls have been made. These were accomplished by one-step polystyrene replicas, and by two-stage plastic and carbon replicas. In both methods, the colloid particles are imbedded in the replica and stripped from the magnetic film. Figure 2 illustrates a replica obtained from a dried pattern. A good collection of particles has occurred on the walls, which gave rise to the bright pattern observed in this particular film. The collapse of the particles and aggregates on drying apparently causes the continuous appearance of the lines of colloid. Colloids which have as a suspending agent a material which gradually thickens as it dries (e.g. Celacol), and eventually produces a durable film, can be used to obtain patterns not distorted by a drying process. Colloids under investigations at present are not of this type, and have been evaporated to dryness before replication.

### 2.3 Protective Overlayers

In addition to modification and continued development of improved colloidal suspensions, considerable effort has been made in the direction of preparing and evaluating protective overlayers on the display films. These films can serve a number of functions, namely: 1) protection of the film from any corrosive action of the suspension; 2) inhibiting absorption or reaction of the colloid particles with the film and acting as a parting layer to prevent immobilization; 3) changing wetting characteristics of the film surface to improve filling procedure; 4) changing the nature of the surfaces to be sealed so that variation of sealing technique is possible.

A number of protective layers were given preliminary evaluation, and these can be divided into the following categories: a) metallic, particularly inert or noble metal films; b) polymer layers; c) other non-metallic films. The best results were obtained with polymer layers such as fluorocarbons and nitro-cellulose, and



Figure 2. Electron micrograph of Polystyrene replica of dried colloid on display film. 3600X

non-metal films such as SiO<sub>2</sub> and carbon. Since SiO<sub>2</sub> films, in several tests, protected units from immobility for up to 4 months, they are considered as a logical choice for more extensive tests. Moreover, SiO<sub>2</sub> films can act as anti-reflection surfaces so that further benefits can result from their use. A large number of films of melt composition 84-16 Ni/Fe were prepared for SiO<sub>2</sub> overlayer tests, and SiO<sub>2</sub> films of desired thicknesses were prepared by evaporation. Coatings consisted of single layer films ranging from 300 to 2000 Å, and multiple layer films having a total thickness of 600 to 2000 Å. Thickness variation was made on a series of films or similar properties, and also in stepwise fashion over the surface of single films. The tests were not conclusive in establishing a definite pattern of "freezing" time; however, a three-layer SiO<sub>2</sub> film of total thickness, 800 Å, produced the optimum freedom from immobilization. In many cases in which freezing did occur, the solutions could be reactivated by slight agitation. The tests on SiO<sub>2</sub> coatings are still in progress and essentially test only the colloid which was used to the greatest extent in filling units. Since the test began, greatly improved non-aqueous suspensions have been developed, and their performance exceeds that of the "standard" colloid, even on unprotected films. Consequently, protective layers will be evaluated using these more recent solutions.

### 3.0 SEALING OF BITTER SOLUTION IN DISPLAY MODULE

A chronological survey of sealing problems from April 1965 shows the following problems: filling units with solution, bubble formation, glass breakage, film attack, and drying of the colloid solution. These are in addition to the immobilization of the colloid discussed already. The technique of filling is described in a previous report.

The first improvement was to find cover glasses (microscope slides) which were 45 mm/50 mm  $\pm$  .002 inch. A. D. Jones Optical Company was able to supply these by cutting off one edge of a larger slide. Previously, there were hand-cut. Since a better bond is formed if the unit, i.e., film and coverglass, can be heated; no colloid is used until this heating step has been performed.

Since the substrate is bent, a reforming or flattening action must be used to obtain as uniform a spacing as is possible - thus pressure is used during initial sealing.

Bubble formation is caused by trapped air or reaction products (film and solution reaction) after the unit is filled. SiO is especially subject to bubble formation.

Bond reliability and spacers were discussed previously. In the past, some attempt to silk-screen channels which would act as spacers was made. It was found that this technique was rather crude for the type of control needed ( $\pm 0.8$  mil). Even present spacers are not always effective, since this is still in the experimental stage.

Most of the effort was placed on filling and sealing techniques, since these needed the most improvement. Although still imperfect, the present technique is the result of a logical approach to the improving of inside dimensions, and appears to be simple and more reliable than the previous filling methods.

It has been observed that bonding life is improved by treatment of the substrate in a sulfuric-chromic acid, bath prior to film deposition.

Glass dimensions were measured and the cover glasses were found to have better dimension tolerances than the substrate glasses. The average dimensions of 10 samples are as follows:

Cover glass:	1.968	+ .001 - .002	1.774	+ .001 - .001
Thickness:	0.388	+ .0018 - .0023	in inches.	
Substrate:	1.970	+ .005 - .005	1.776	+ .004 - .004
Thickness	.006	+ .0015 - .0015	in inches.	

Most of the sealing work during the period consisted of using previously developed techniques to seal display modules for colloid life tests. Although the present Epon epoxy bond appears satisfactory, a polyester cement with increased ability to withstand immersion is being tested. Bonding techniques using soluble silicates and transparent epoxy material are also under consideration. The use of a metal strip or bond, of non-magnetic alloy is planned to increase bond strength and decrease bond dimensions, and a mask for photo-etching these strips has been prepared.